Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Engineering 47 (2012) 1149 – 1152

Procedia Engineering

www.elsevier.com/locate/procedia

Proc. Eurosensors XXVI, September 9-12, 2012, Kraków, Poland

A Miniaturized Catalytic Gas Sensor for Hydrogen Detection Containing a High Porous Catalytic Layer Formed by Dry Lift-Off

E. Brauns[a] *, T. Seemann[b], V. Zoellmer[b], W. Lang[a]

[a] *IMSAS (Institute for Microsensors, -actuators and -systems), University of Bremen, Otto-Hahn-Allee NW1, 28359 Bremen, Germany*

[b] *Fraunhofer IFAM (Fraunhofer Institute for Manufacturing Technology and Applied Materials Research), Wiener Straße 12, 28359 Bremen, Germany*

IMSAS and Fraunhofer IFAM are part of the Microsystems Center Bremen (MCB)

Abstract

This paper presents a miniaturized catalytic gas sensor for hydrogen detection, based on a sputtered high porous catalytic platinum layer, formed by dry lift off. It provides the possibility to structure these sensitive materials without using any chemicals or solvents. Due to the miniaturized device combined with this porous catalytic layer it is possible to reach a high sensitivity and a low response time [1], which offers other operating modes, e.g. alternating input signal modulation [2]. A new sensor design provides a better controlling of the catalytic temperature, which improves the stability of the catalytic structures. A sensitivity of about 1.8 mV / 100 ppm is reached.

Keywords: gas sensor; catalytic; hydrogen; high porous; platinum; lift-off;

1. Introduction

Catalytic gas sensors are well known as thermal devices for detection of combustible gases in air, notably in applications for safety systems. The measuring principle is to heat up a catalyst to its operating temperature. If a combustible gas (e.g. hydrogen as shown here) is provided in the environment, it will react with oxygen. The resulting exothermic reaction leads to a higher temperature which is measurable.

* Corresponding author. Tel.: +49 (0)421 218-62576; fax: +49 (0)421 218-98-62576.
E-mail address: ebrauns@imsas.uni-bremen.de.

doi:10.1016/j.proeng.2012.09.355

Typical catalytic gas sensors are based on a fine mechanic porous element, coated by a catalytic layer. Due to their great dimensions, high power consumption and high response time, these sensors are inefficient for most fields of application.

Micro technological based sensors were developed to reduce those common problems. The decrease of dimensions reduces the power consumption and primarily improves the response time. This allows different operating modes, e.g. fast time varying controlling [2]. This approach leads to an advanced controlling potential to analyze more gas characteristics, e.g. gas quality and composite.

A membrane sensor and a porous catalytic layer is used here to increase the sensitivity and to decrease the operating temperature and thereby the power consumption. The enlarged catalytic surface allows high sensibility to measure small gas concentrations. The catalyst's operating temperature of 100°C is kept constant to decrease thermal load to its layer. Sensor's information is displaced to the reference. As temperature sensing element, thermopiles are used. The advantage of these elements compared to a resistive measurement is to reduce the required electronics for reading the information.

2. Technological Approach

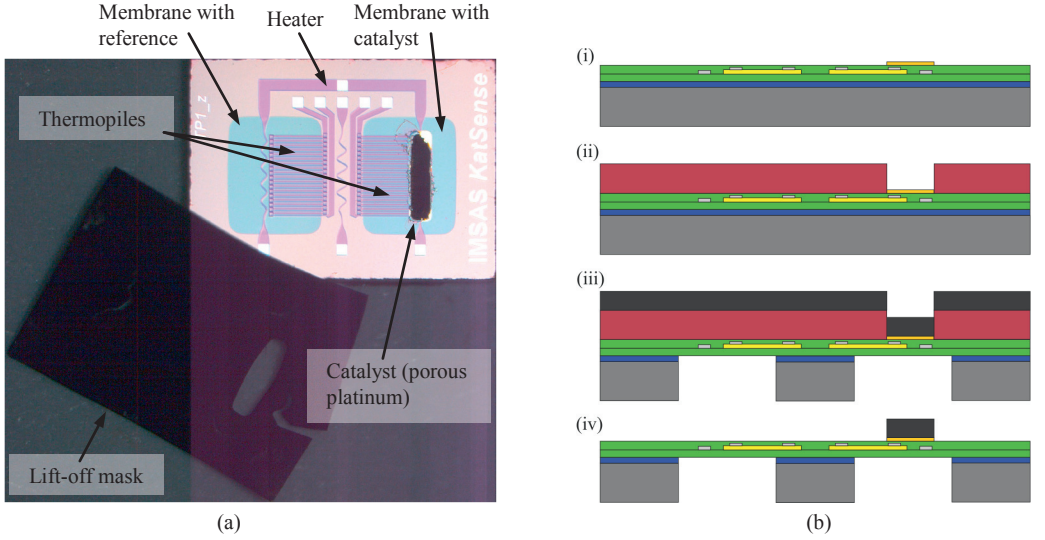


Fig. 1 (a) catalytic gas sensor and its lift-off mask for structuring the high porous catalytic layer. The design provides two separated membranes to decrease interaction between reference and catalyst. Thermopiles measure the temperature between substrate (environement) and membrane; (b) schematic view of the process: i) functional structures with an adhesion layer (Au) for the catalyst, ii) after coating an anti adhesion layer, the polyimide is laminated, exposed and developed, iii) releasing membranes by DRIE, separating sensors and depositing the high porous catalytic layer by using PVD, iv) forming catalyst by stripping polyimide.

2.1. Device

Functional structures are realized on two membranes for both catalyst and reference to reduce interaction. A heater is placed over both membranes to heat the catalyst up to its operating temperature (Fig. 1 a). Reaction of hydrogen with oxygen to water leads to a higher temperature at the catalyst. The temperature is measured by thermopiles, difference can be interpreted as the hydrogen's concentration.

The heater is contacted at three points to realize a selective heat controlling. This will prevent the catalyst's temperature from increasing above the operating temperature and damaging the catalyst. Controlling of the temperature is done by a digital circuit, utilizing the temperature behavior of thin

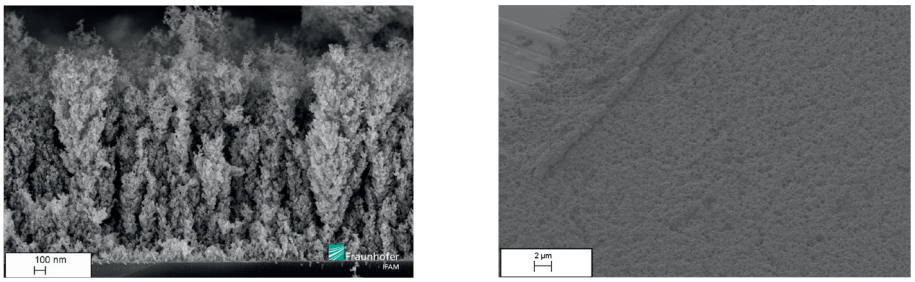
resistors (thermistor). The whole heater is supplied by the same power, whereas the temperature is measured and controlled at the catalyst only. Temperature injection of catalytic reaction leads to a lower demand of power to keep catalyst's temperature constant. Temperature of the reference will decrease. This indirect measurement compared to the direct measurement of power has the advantage of a higher resolution, a higher measuring range and an independence of temperature fluctuation in the environment.

To protect the functional layers from influences of the catalysts temperature, they are embedded and passivated in a 600 nm pinhole free low stress silicon rich silicon nitride membrane made by LPCVD (low pressure chemical vapor deposition). As first material for thermopiles, *in-situ* p-doped polysilicon is used to reach a high Seebeck coefficient. The second material and heater's material is tungsten titanium. A diffusion barrier made of titanium nitride is used to avoid diffusion effects at the junctions of the thermopiles [3]. A schematic view of the sensor's cross section is shown in Fig. 1 b.

2.2. Catalyst

For the structuring of the catalytic layer, a dry lift-off method was used. After completion of the functional structures, polyimide (Conformask®) was deposited to form the lift-off mask. For a volitional worse adhesion, the wafer was coated with an anti adhesion layer (BGL-GZ-83) before, so later the polyimide can easily be removed by using tweezers. Then the dry lift-off mask was laminated, exposed and developed. Accordingly, the membranes were etched by using DRIE and the sensors were separated. Finally, the catalytic Layer was deposited by PVD and structured by removing the lift-off mask (Fig. 1 b).

To adjust the porosity, a modified magnetron radio frequency sputtering process with a high pressure was used as shown in [4]. A porosity of up to 92 % can be obtained, while the used porosity is an agreement of stability and sensitivity. In this case, a porosity of about 80% was used (Fig. 2).



(a) (b)

Fig.2 (a) SEM-picture of the porous catalytic layer (cross section) with a porosity of about 90%; (b) Overview of the catalyst.

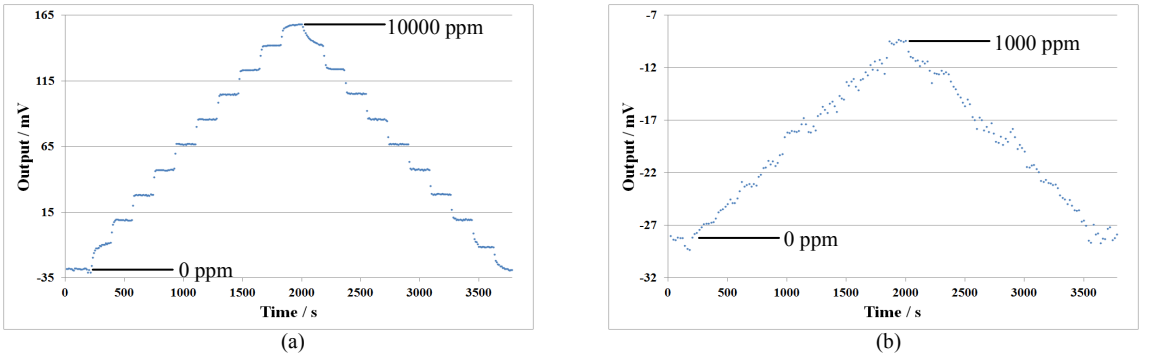
3. Measurements

Measurements with the sensor were made while varying the hydrogen concentration stepwise. In spite of using synthetic air, every measurement was performed with a humidity of at least 15%. Humidity and temperature of the environment were measured by an additional sensor inside the test chamber. As operating temperature, 100°C was selected, to prevent inclusion of water at the porous catalyst, induced as reaction product or by humidity. Lower temperatures drastically decrease the sensitivity. A power consumption of about 20mW was determined, while it decreases with a rising gas concentration.

The hydrogen concentration has been changed gradually in 1000 ppm steps and for investigation of the resolution in 100 ppm steps. The result can be seen in Fig. 3. Caused by an unstable controlling of the temperature, very noisy signals were obtained. It is assumed that a better controllable adjustment should offer resolutions down to 10 ppm. A sensitivity of about 1.8 mV / 100 ppm was reached.

By changing the gas mixture with a valve directly at the reactors inlet, a 90%-response time of about 1.5 s was determined, while this response time includes the time of filling the reactor. The actual response time is assumed to be << 1 s.

Long-term stability and influence of humidity was analyzed. Obviously a higher humidity leads to a lower sensitivity. Under constant gas atmosphere for several hours, the sensor begins to deactivate. After 3 days, the sensor's signal stabilizes at very low sensitivity, thus the advantage of porous structure is lost. It is assumed, that the long-term stability can be improved by using a composition of metals.



(a) (b)

Fig. 3 (a) Output signal from a sensor while changing the hydrogen concentration gradually between 0 ppm and 10000 ppm in 1000 ppm steps; (b) Output signal while changing the hydrogen concentration gradually between 0 ppm and 1000 ppm in 100 ppm steps. A sensitivity of abou 1.8 mV / 100 ppm is reached. The sensitivity depends on the thickness of the catalytic layer, a higher thickness will increase the sensitivity. Here, a thickness of about 4 µm is used.

4. Conclusion and Outlook

A catalytic gas sensor for hydrogen detection based on high porous platinum has been developed. Therefore, a membrane sensor was coated with high porous platinum, which was structured by using a dry lift-off method. A sensitivity of about 1.8 mV / 100 ppm was demonstrated, while it is assumed that a significant smaller resolution and a higher sensitivity can be reached, with a more stable controlling of the heater and a higher thickness of the catalytic layer.

Future tasks are based on determination of the exact response time and on improvement of long-term stability by using compositions of metals for high porous catalytic layer to avoid agglomeration effects.

Acknowledgements

The financial support was given by the Innovation Cluster "Multifunctional Materials and Technologies" (MultiMaT) from the state of Bremen via the European Regional Development Fund ERDF, the Fraunhofer society and industry in equal parts.

References

[1] H. Sturm, E. Brauns, T. Seemann, V. Zoellmer, W. Lang. A Highly Sensitive Catalytic Gas Sensor for Hydrogen Detection Based on Sputtered Nanoporous Platinum. *Procedia Engineering* 5; 2010, p. 123-126

[2] R. Aigner, M. Dietl, R. Katterloher, V. Klee. Si-Planar-Pellistor: Designs for Temperature Modulated Operation. *Sens. Actuat. B-Chemical* 33; 1996, p. 151-155

[3] R. Buchner, C. Sosna, M. Maiwald, W. Benecke, W. Lang. A High-Temperature Thermopile Fabrication Process for Thermal Flow Sensors. *Sens. Actuat. A-Physical* 130-131; 2006, p. 262-266

[4] P.J. Kelly, J. O'Brien, R.D. Arnell: The production of porous and chemically reactive coatings by magnetron sputtering. *Vacuum* 74; 2004, p. 1-10